Video STM Studies of Adsorbate Diffusion at Electrochemical Interfaces

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Direct *in situ* studies of the surface diffusion of isolated adsorbates at an electrochemical interface by high-speed scanning tunneling microscopy (video STM) are presented for sulfide adsorbates on Cu(100) in HCl solution. As revealed by a quantitative statistical analysis, the adsorbate motion can be described by thermally activated hopping between neighboring adsorption sites with an activation energy that increases linearly with electrode potential by 0.50 eV per V. This can be explained by changes in the adsorbate dipole moment during the hopping process and contributions from coadsorbates.

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Adsorbate diffusion on clean surfaces under ultrahigh vacuum (UHV) conditions is a well characterized process [1,2]. Of particular fundamental importance is the case of low adsorbate coverage, where adsorbate-adsorbate interactions can be ignored and only the diffusion of isolated adsorbates has to be considered (''tracer diffusion''). The most detailed experimental data have been obtained from direct studies of the adsorbate motion via high-resolution microscopic techniques, such as field ion microscopy [1] and, more recently, scanning tunneling microscopy (STM) [2–7]. As verified by such studies, tracer diffusion of simple atomic adsorbates can often be described as a thermally activated hopping between the energetically preferred adsorption sites on the surface with an activation energy (''diffusion barrier'') given by the spatial modulation of the adsorption energy in the surface plane and a preexponential factor (''attempt frequency''), which is typical of the order of the adsorbate vibration frequencies.

In contrast, the more complex case of adsorbate diffusion at metal-electrolyte interfaces or, more general, at solid-liquid interfaces is considerably less understood. Qualitatively, a pronounced influence of the liquid phase and the potential of the metal electrode on the decay of surface features [8–10], the morphology of deposits [11], and the order of adsorbate layers [12] was observed, suggesting that the electrochemical environment strongly affects the mobility of adsorbates. However, apart from metal self-diffusion, which was investigated in detailed studies of step fluctuations and island coarsening (see Ref. [9] for an overview), no quantitative diffusion data have been obtained. Furthermore, tracer diffusion studies by atomic-resolution microscopy have up to now not been reported at all for adsorbates at solid-liquid interfaces. This is largely caused by the high surface mobility of most adsorbates in the available temperature window and the lack of *in situ* microscopic methods with sufficiently high temporal resolution.

Here we present a first direct study of adsorbate tracer diffusion at an electrochemical interface by *in situ* video STM. The system selected for these measurements, adsorbed sulfide (coverage 0.005 to 0.0015 ML) on Cu(100) in $0.01M$ HCl solution, is especially well suited due to the following reasons: First, sulfide is a particularly strongly bound adsorbate and on the highly corrugated Cu(100) surface sufficiently immobile for direct video STM observations. Second, the Cu(100) surface is covered in the entire studied potential range by an ordered $c(2 \times 2)$ chloride adlayer [13,14], which results in a very-well-defined, potential-independent environment of the sulfide adsorbates. Specifically, sulfide can be inserted into this lattice (see below), since it easily replaces the less strongly chemisorbed $\mathrm{Cl_{ad}}$ from the surface even at low concentrations [15]. In the following, results of a quantitative study of the sulfide adsorbate motion as a function of potential and temperature are discussed and rationalized using a simple model.

The experiments were performed at controlled temperature (277 to 296 K) and potential ($-0.52V_{\mathrm{SCE}}$ to $-0.36V_{\mathrm{SCE}}$), using a homebuilt video STM for *in situ* measurements in an electrochemical environment [16]. STM video sequences 1 to 3 min long were recorded at image acquisition rates of 10 to 30 images per second in ''constant height'' mode using Apiezon coated W tips. Prior to the measurements, the Cu(100) sample was electropolished in orthophosphoric acid (see Ref. [13]) and immersed into an $0.01M$ HCl solution, prepared from suprapure HCl (Merck) and ultrapure water. Then sulfide was dosed onto the surface by adding 5 μl of 12 μM $\mathrm{Na_2S}$ solution to the STM cell, resulting in an $\mathrm{S_{ad}}$ coverage of 0.005 to 0.015 ML. Potentials were measured by a Cu wire, calibrated vs a saturated calomel electrode (SCE). STM experiments were started ≈ 30 min after dosing $\mathrm{S_{ad}}$.

In the STM images the sulfide adsorbates appear as isolated white protrusions located at positions of the $c(2 \times 2)$ lattice [Fig. 1(a), full video sequences are provided in [17]]. Obviously, each $\mathrm{S_{ad}}$ replaces one $\mathrm{Cl_{ad}}$ from a lattice position at these low coverages (ordered sulfide adlayers with different structures are observed only at higher coverages [15]). The hopping of isolated $\mathrm{S_{ad}}$ adsorbates between $c(2 \times 2)$ lattice sites can be clearly observed in the video

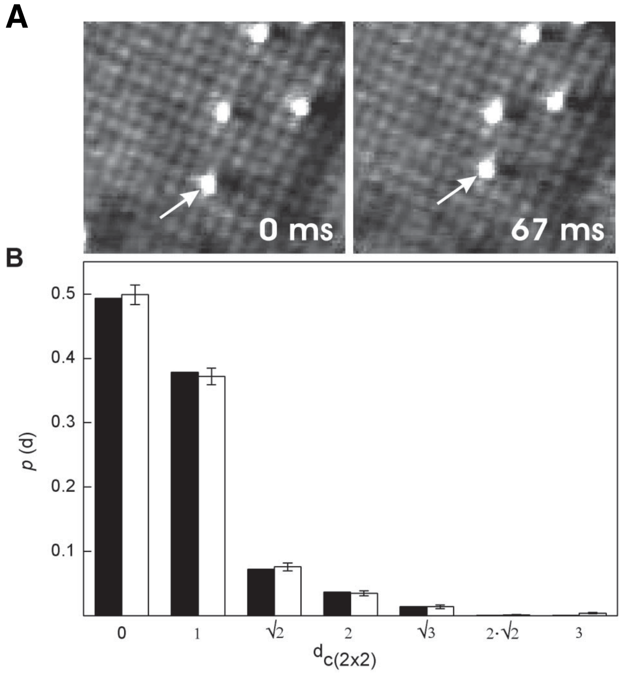

FIG. 1. (a) Two successive *in situ* STM images (40×40 Å^2) from a video sequence recorded at 15 images/s on Cu(100) in $0.01M$ HCl solution at $-0.32V_{\mathrm{SCE}}$, showing the hopping diffusion of isolated sulfide adsorbates (coverage 0.005 ML) on the $c(2 \times 2)$-Cl covered Cu surface. (b) Experimental jump distribution function $p(d)$ (open bars), obtained by analyzing 900 images of a video sequence recorded at 10 images/s at $-0.52V_{\mathrm{SCE}}$ and a temperature of 293 K, and best fit to a 2D continuous time random walk model (black bars). From the fit a hopping rate of $\upsilon_S = 7.8 \pm 0.2$ s^{-1} is obtained.

sequences [example marked by arrow in Fig. 1(a)]. The hopping rates depend on potential and temperature and are in the range of 0.1 to 10 s^{-1} under the chosen experimental conditions. At very low rates only displacements by one $c(2 \times 2)$ lattice constant $d_{c(2\times2)} = 3.6$ Å are found, indicating that diffusion occurs by $\mathrm{S_{ad}}$ jumps between neighboring adsorption sites. This process must involve either place exchange of $\mathrm{S_{ad}}$ with the $\mathrm{Cl_{ad}}$ in the corresponding neighboring site or $\mathrm{Cl_{ad}}$ desorption and subsequent rapid $\mathrm{Cl_{ad}}$ adsorption into the $c(2 \times 2)$ site vacated by the hopping $\mathrm{S_{ad}}$. Furthermore, the observations reveal a significant enhancement of the $\mathrm{S_{ad}}$ diffusion in the presence of neighboring sulfide adsorbates. For this reason, the quantitative analysis of the diffusion process was restricted to $\mathrm{S_{ad}}$ adsorbates with a minimum spacing $>4d_{c(2\times2)}$ to the nearest neighboring $\mathrm{S_{ad}}$. To ensure that the measurements were not influenced by the STM tip, systematic studies were performed, which found that the diffusion rates were affected only at tunneling currents >9 nA.

To determine the hopping frequency υ_{S} jump distribution functions were generated, which give the probability p for a specific $\mathrm{S_{ad}}$ displacement d between two successive STM images [Fig. 1(b), white bars]. For this, the positions of all sufficiently isolated $\mathrm{S_{ad}}$ (see above) were measured in every image of the video sequence, and their displacement d in the subsequent image was determined. The number of observations for each d, averaged over symmetrically equivalent sites and normalized by the total number of observations (typically 2000 to 3000) gives the displacement probability $p(d)$. For hopping rates considerably smaller than the recording rates (i.e., displacements to neighbor sites only), υ_{S} is directly given by the number of displacements per second. At higher rates υ_{S} was obtained by fits of the experimental jump distribution functions using a 2D continuous time random walk model with jumps between neighboring sites only [Fig. 1(b), black bars] [18]. This model, which contains only υ_{S} as a free parameter, very well describes the experimental data, confirming that diffusion occurs via sequential jumps between neighbor sites even at higher diffusion rates.

As shown in Fig. 2, the sulfide hopping rates determined by this method depend strongly on potential and temperature. Similar to the case of diffusion at the metal-vacuum interface, temperature-dependent measurements at constant potential are well described by an Arrhenius law [Fig. 2(a)]. Consequently, attempt frequencies and diffusion barriers can be obtained from fits of the data in Fig. 2(a) (indicated by solid lines). Although comparable data for $\mathrm{S_{ad}}$ diffusion on Cu(100) under UHV conditions do not exist, the resulting υ_0 and E_d are of comparable magnitude as those found for similar adsorbate systems at metal-vacuum interfaces [2]. The attempt frequency for hopping is (within the experimental error) independent of potential with a value of $\upsilon_0 = (2.35 \pm 0.35) \times 10^{12}$ s^{-1}. However, the diffusion barrier E_d linearly increases with potential [Fig. 2(b)], resulting in a change in the hopping rates of approximately 1 order of magnitude per 100 mV. This linear potential dependence of the diffusion barrier is also clearly visible in a more extensive data set, obtained at room temperature [Fig. 2(c)], where a nearly perfect exponential decrease of υ_{S} with potential is found, in perfect quantitative agreement with the temperature-dependent study. All the data can hence be summarized by a diffusion barrier consisting of a constant term (whose value depends on the choice of the reference electrode) and a term depending linearly on the potential ϕ, i.e., $E_d = E_0 + a\phi$, with $E_0 = (0.938 \pm 0.005)$ eV and $a = (0.504 \pm 0.013)$ eV$/V_{\mathrm{SCE}}$.

As is shown in the following, possible contributions to the potential-dependent part of E_d—a genuine effect of the electrochemical environment—can come from the sulfide diffusion barrier, the Gibbs free energy of adsorption of the chloride coadsorbate, and the coverage of vacancies in the $c(2 \times 2)$ Cl adlayer, which all can cause a linear potential dependence. Origin of the latter is in all three cases the electrostatic energy of the adsorbates in the electric field $\vec{F}_{\mathrm{DL}}$ of the electrochemical double layer at the electrode surface. Since the sulfur as well as the chloride anions

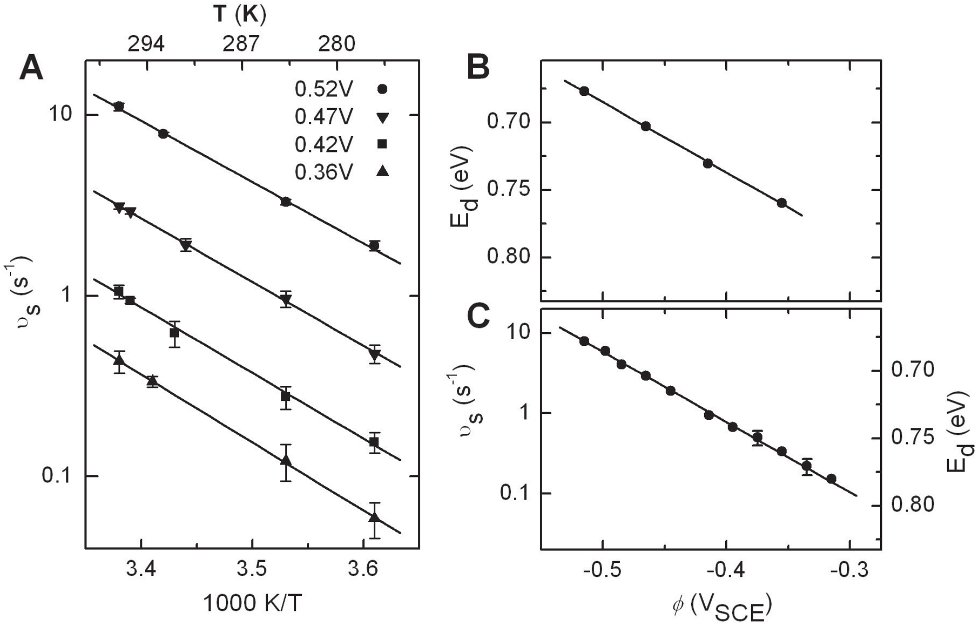

FIG. 2. (a) Sulfide hopping rates as a function of temperature at 4 different potentials. (b) Potential-dependent diffusion barrier $E_d(\phi)$, obtained from Arrhenius fits (solid lines) of the data in (a). (c) Potential dependence of the S_{ad} hopping rates at 296 K (if not shown, error bars are smaller than symbol size). The corresponding diffusion barriers $E_d(\phi)$ (right scale) were calculated for a fixed attempt frequency $\upsilon_0 = 2.35 \times 10^{12}$ s^{-1}.

retain a small negative partial charge after adsorption, they are more strongly bound to the electrode at more positive potentials, which also affects the adsorbate mobility. More rigorously, using the surface dipole moment $\vec{p}_{ad}$ pointing from the adsorbate to its image charge in the metal substrate, the free energy of adsorption can be written as $G_{ad} = G^0_{ad} - \vec{p}_{ad}\vec{F}_{DL} = G^0_{ad} + (p_{ad}/\varepsilon_0)\sigma$, where σ is the surface charge density on the electrode. This is particularly easy to see for the structurally very-well-defined system studied here, where the adsorbates are located in a (solvent-free) close-packed layer and changes in the electric field at the interface are predominantly associated with changes in the coverage of (solvated) Cl$^-$ ions above this adsorbate layer and corresponding changes in the electronic surface charge density of the underlying Cu substrate [19]. However, as shown very recently the derived expressions should also hold more generally [10]. Assuming that p_{ad} is independent of the potential within the potential regime of the $c(2 \times 2)$ phase and introducing the differential capacitance $C_d = d\sigma/d\phi$, which has an approximately constant value of 25 μF/cm^2 in this potential range [14], a linear potential dependence with a slope $dG_{ad}/d\phi = p_{ad}C_d/\varepsilon_0$ results.

First, the effect of the electrostatic energy contribution $p_{ad}C_d/\varepsilon_0\phi$ on the sulfide diffusion barrier is considered. Since the surface dipole moment depends on the electronic and geometric structure of the adsorption complex, it should differ for an S_{ad} adsorbed in the preferred fourfold-hollow site and an S_{ad} in the activated state corresponding to the diffusion barrier. More precisely, an increase of p_{ad} in the (lower coordinated) activated state is expected. The difference of these energies, which equals E_d if the effects of coadsorbed species are neglected, should therefore linearly increase with increasing potential. Hence, in this model the potential-dependent mobility is directly related to the change in the S_{ad} adsorption geometry and charge state during the hopping process, resulting in an increasing S_{ad}-substrate interaction with increasing electric field at the interface.

Second, the potential-dependent S_{ad} mobility may be (partly) caused by the Cl coadsorbates, for which a similar electrostatic energy contribution to the free energy of adsorption exists. Since the hopping process involves the displacement of a neighboring Cl$_{ad}$, this energy should contribute as well to the effective diffusion barrier. An upper limit for the potential dependence caused by this effect can be estimated using data obtained for $c(2 \times 2)$ Cl$_{ad}$-covered Cu(100) under UHV conditions [20], from which a Cl dipole moment of $p_{ad,Cl} = 1.3 \times 10^{-30}$ Cm can be calculated. This results in $dG_{ad,Cl} = 0.20$ eV$/V_{SCE}$, i.e., considerably less than the experimental value found for S_{ad} in this study. Furthermore, since adsorbate surface dipole moments in the electrochemical environment are usually significantly reduced due to contributions of the solvent molecules, $dG_{ad,Cl}/d\phi$ most probably is even lower. Strongly chemisorbed coadsorbates could also affect the surface diffusion by completely blocking the S_{ad} hopping to neighbor sites. In this case hopping will occur only when one of the neighboring $c(2 \times 2)$ lattice sites is vacant. Consequently, the hopping rate should be proportional to the vacancy density in the Cl adlayer, which exponentially decreases with potential [21]. If the surface dipole moments of Cl adsorbates surrounding the vacancy remain unchanged, the same slope of $0.20\ \mathrm{eV}/V_{\mathrm{SCE}}$ as found above results. However, relaxation of the dipole moments in the vicinity of vacancies is likely, which should reduce this slope. In summary, coadsorbates very likely contribute to the potential dependence of the sulfide diffusion, but cannot account alone for the observed effect.

Our results demonstrate that direct quantitative studies of adsorbate diffusion at solid-liquid interfaces are possible, which allows us to clarify these elemental processes in unprecedented detail. As shown for the structurally well-defined model system investigated here, the basic model developed for adsorbates on metal surfaces under UHV conditions remains valid; i.e., diffusion of isolated adsorbates at electrochemical interfaces is well described by thermally activated hopping. However, the electrostatic energy of the adsorbates surface dipole moments in the electric field of the electrochemical double layer causes a potential-dependent contribution to the diffusion barrier. The almost perfectly linear relationship observed in our study indicates that higher order effects, such as the dependence of the dipole moments on the potential, can be neglected under the employed experimental conditions. According to the above analysis, the potential dependence of the diffusion barrier primarily results from the variation in the S_{ad} dipole moment (i.e., charge state and adsorption geometry) during the hopping process, although a smaller contribution caused by the Cl coadsorbate is likely. A similar potential-dependent surface diffusion can therefore be expected for all (partly charged) adsorbates at electrochemical interfaces. The precise contribution of the diffusing species and the surrounding coadsorbates will be elucidated in future systematic studies of related adsorbate systems. Moreover, the detailed data obtainable by video STM, from which not only tracer diffusion but also adsorbate-adsorbate interactions can be extracted [4], can be directly compared with the results of theoretical studies using *ab initio* methods, which should promote the development of better quantum chemical models of this complex interface.

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